

Surface modification of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode by coating with $\text{SiO}_2\text{-TiO}_2$ composite^①

YU Xiao-yuan(禹筱元)^{1, 2}, HU Guo-rong(胡国荣)¹, PENG Zhong-dong(彭忠东)¹,
XIAO jin(肖劲)¹, CHEN Zhao-yong(陈召勇)¹, LIU Ye-xiang(刘业翔)¹

(1. School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China;
2. School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China)

Abstract: The cycling characteristics and low specific capacity of LiMn_2O_4 have always been the greatest obstacle to its commercialization. For the improvement of cycle performance, the surface of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ was coated with very fine $\text{SiO}_2\text{-TiO}_2$ composite prepared by sol-gel method. The structure and morphology of the coating materials were investigated by X-ray diffraction (XRD) and scanning electron microscope (SEM). The electrochemical performances of uncoated and $\text{SiO}_2\text{-TiO}_2$ coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ spinel at 25 °C and 55 °C were studied with a voltage range of 3.0 - 4.35V and a current density of 0.1 mA/cm². There is a slight decrease in the initial discharge capacity of coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ (119 mA·h/g) compared with that of uncoated (123 mA·h/g). However the cycle ability of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ coated by $\text{SiO}_2\text{-TiO}_2$ is improved. It is proposed that surface treatment is an effective method to improve the cycle performance of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$. The surface modification is successful in minimizing the harmful side reactions within the batteries by placing a protective barrier layer between the oxidizing cathode material and the liquid electrolyte.

Key words: lithium-ion batteries; surface modification; $\text{SiO}_2\text{-TiO}_2$ coating; $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathode

CLC number: TM 911.1

Document code: A

1 INTRODUCTION

Since the first commercialization by Sony Corporation in the early 1990s, the lithium-ion battery (LIB) has become a major product to dominate the market for small rechargeable batteries. Furthermore, LIBs are expected to be used as a large-scale energy storage device for electric vehicles (EV)^[1].

Though various types of cathode materials such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and substituted transition metal oxides are currently used in commercialized LIBs^[2,3], LiCoO_2 in these cathode materials is most widely used because of its excellent cycle life and rate capacity. Moreover, cobalt is a relatively rare and very expensive transition metal, attention has been paid to LiMn_2O_4 to take advantage of its low cost and environmental friendly nature over LiCoO_2 . But the cycling characteristics and low rate capacity of LiMn_2O_4 have been the greatest obstacle to its commercialization^[4,5].

Some improvements of the spinel LiMn_2O_4 were made by controlling the specific area, the Li stoichiometry and the annealing conditions. And a significant effort was devoted worldwide to understand the mechanism of the capacity fade, which has been con-

tributed to the Jahn-Teller distortion caused by the presence of Mn^{3+} , Mn dissolution, electrolyte decomposition^[6-9]. Two major paths to improvement have been pointed out. 1) Structure modifications^[10-12]: Cation substitution and subsequent control of Mn oxidation state were successfully used to enhance the room temperature cycling of $\text{LiMn}_{2-y}\text{M}_y\text{O}_4$ (M = Li, Co, Cr, Mg, Fe) through controlling the average oxidation state of the manganese cation. The increased concentration of tetravalent manganese resulted in the improved cycling stability of the spinel. Amatucci et al^[13] considered the anion substitution of oxygen for fluorine and studied the effect of fluorine substitution on the chemical and structural stability of the spinel $\text{LiM}_x\text{Mn}_{2-x}\text{O}_{4-z}\text{F}_z$ (M = Li, ...). 2) Surface modification^[14-16]: Based on the fact that Mn dissolution occurs at the interface between electrolyte and LiMn_2O_4 , Tarascon et al^[3] reported a simple way to improve the poor cycle stability at elevated temperature through fabricating a material with low surface area. Particle coating was achieved by encapsulating the spinel surface either with a lithium boron glass or other Li-bearing oxide glasses. An alternative method was the removal of the LiMn_2O_4 active surface centers through a complexing reaction with acetylacetone (AA).

① **Foundation item:** Project(02JJY2081) supported by the Natural Science Foundation of Hunan Province, China

Received date: 2004 - 01 - 05; **Accepted date:** 2004 - 04 - 13

Correspondence: YU Xiao-yuan, PhD; Tel: + 86-731-8830474; E-mail: yxy7021@mail.csu.edu.cn

Although these approaches have not completely solved the high temperature issue intrinsic to LiMn_2O_4 , at least it pointed out the importance of a better control of the electrode/electrolyte interface through the design of new solid/solid or solid/liquid interface. Based on the same concept, successful modifications of the spinel surface layer by treating the powders with alkali-hydroxide solutions followed by a high temperature calcination produced spinel powders with enhanced storage performances.

In this paper, a sol-gel method was applied to coat a thin composite layer of $\text{SiO}_2\text{-TiO}_2$ on the surface of the spinel $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ particles. The surface-modified $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cathodes showed good electrochemical charge/discharge cycling performance.

2 EXPERIMENTAL

The powder samples of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ were synthesized via a conventional solid-state reaction which used the stoichiometric amounts of electrodeposited manganese dioxide (EMD), LiCO_3 , CoCO_3 . They were mixed thoroughly by ball-milling. The mixture precursor was heated to $600\text{ }^\circ\text{C}$ and calcined for 18 h at $600\text{ }^\circ\text{C}$, then calcined for 18 h at $750\text{ }^\circ\text{C}$, and cooled slowly to room temperature. The $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powder was obtained.

The approach for applying coating via sol-gel method was as follows. The coating precursors of ethyl silicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$) and tetrabutyl titanate ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) (The molar ratio of $\text{Si}(\text{OC}_2\text{H}_5)_4$ to $\text{Ti}(\text{OC}_4\text{H}_9)_4$ is 1:1) were dissolved in ethanol, then $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powder was added to this coating solution so that the total amount of the coating solution corresponded to 1% (mass fraction) of the $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powders used, and a constant stirring was followed. Then it was gently heated to $70\text{ - }80\text{ }^\circ\text{C}$ until the solvent was completely evaporated. During the course of the process, $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ were first hydrolyzed into alkoxides or oxides through reaction with H_2O in the atmosphere. The powders were then retained at $500\text{ }^\circ\text{C}$ for 10 h. Finally the mixture was naturally cooled to room temperature, and the $\text{SiO}_2\text{-TiO}_2$ coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ was prepared.

The morphology change of the powders was characterized with a scanning electron microscope (SEM, KYKY-2800). The surface composition of the powders was analyzed using a scanning electron microscope equipped with energy spectrum (SEM, KYKY-2800). X-ray diffraction (XRD, Japan, D/Max-RB) using $\text{CuK}\alpha$ radiation was used to identify the crystalline.

The electrochemical charge-discharge tests were done using the cathode prepared with the mixture of

80% (mass fraction) $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ or surface treated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$, 10% acetylene black (AB) and 10% polytetrafluoroethylene (PTFE). The separator was a Celgard 2400 microporous polyene membrane. The lithium metal was used as anode in this study. The electrolyte was 1.0 mol/L $\text{LiPF}_6/\text{EC} + \text{DEC}$ (1:1, volume ratio). The cells were assembled in a glove box filled with ultrapure argon gas. The charge-discharge cycling was galvanostatically performed at constant current density of 0.1 mA/cm^2 with a voltage range of $3.0\text{ - }4.35\text{ V}$ (vs Li/Li^+) using a LAND CT2001A computer-controlled battery testing system at $20\text{ }^\circ\text{C}$ and $55\text{ }^\circ\text{C}$, respectively.

The cyclic voltammetry curves of the modified powders were measured by the microelectrode method on Model 273A Potentiostat/Galvanostat controlled by computer using M270 software. The working microelectrode was made by filling the powders into a microcavity at the tip of a Pt microdisk electrode. A suitable lithium sheet was used as both counter electrode and reference electrode.

3 RESULTS AND DISCUSSION

3.1 Physical properties

Fig. 1 shows the X-ray diffraction patterns of the uncoated and coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powders. The pattern of uncoated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powders indicates that the material is pure spinel phase. It can be observed that the pattern of the surface-treated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powders is almost the same as that of uncoated one. The absence of any other signals in the spectra indicates that the coated $\text{SiO}_2\text{-TiO}_2$ is probably not crystal, but amorphous in nature.

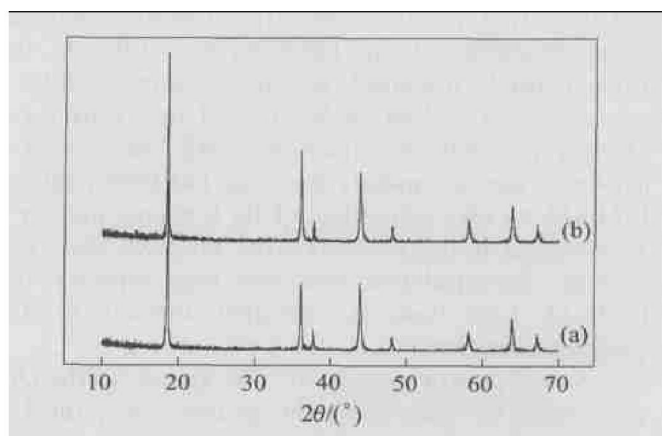


Fig. 1 XRD patterns of uncoated (a) and $\text{SiO}_2\text{-TiO}_2$ coated (b) $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$

Fig. 2 shows the surface morphologies of the uncoated and surface-modified $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ with $\text{SiO}_2\text{-TiO}_2$ composite. The surface morphology of the uncoated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ is very clean and smooth without any foreign phases. In comparison, the sur-

face morphology of the surface-modified powders is blurry, and most of the angular features have been round.

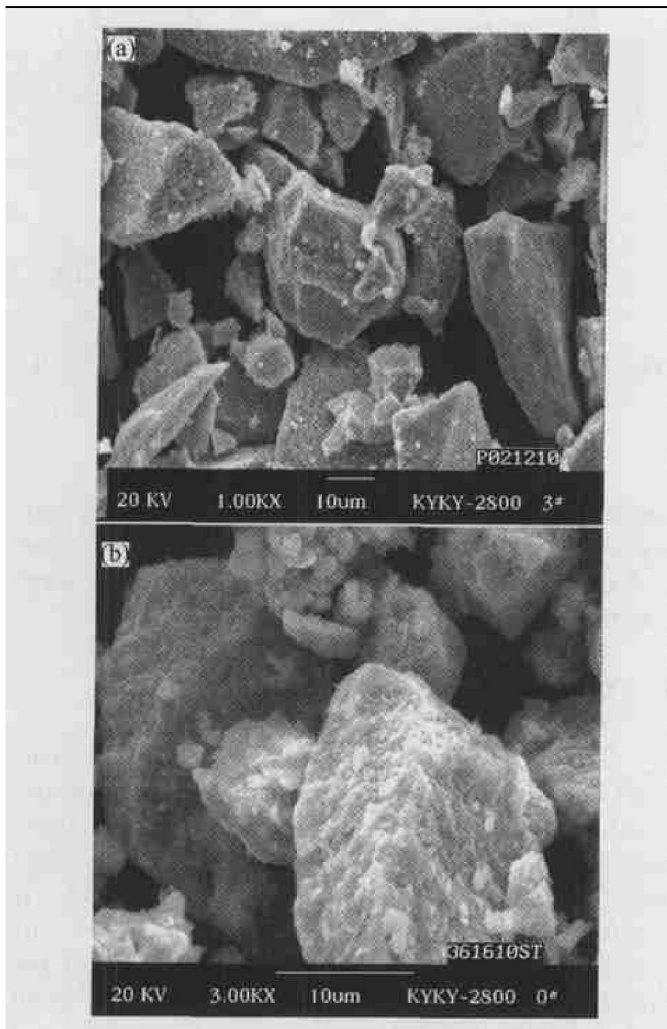


Fig. 2 SEM morphologies of uncoated(a) and $\text{SiO}_2\text{-TiO}_2$ coated(b) $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$

The crystalline grains are obviously coated with a lot of infinitely small flakes. The above modification in morphology may be the result of presence of a $\text{SiO}_2\text{-TiO}_2$ coating.

The surface composition of the powders was analyzed by using EDS, as shown in Fig. 3.

3.2 Electrochemical performance

The electrochemical performance of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ and $\text{SiO}_2\text{-TiO}_2$ coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ at temperature of $25\text{ }^\circ\text{C}$ was tested in Li half-cell. The typical charge-discharge curves of different samples at a current density of 0.1 mA/cm^2 are presented in Fig. 4. The first discharge rate capacity of uncoated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ is $123\text{ mA}\cdot\text{h/g}$ with a two-step voltage profile. The $\text{SiO}_2\text{-TiO}_2$ coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ behaves similarly, as far as the shape of discharge is concerned. There is some slight decrease in the discharge capacity (to $119\text{ mA}\cdot\text{h/g}$)

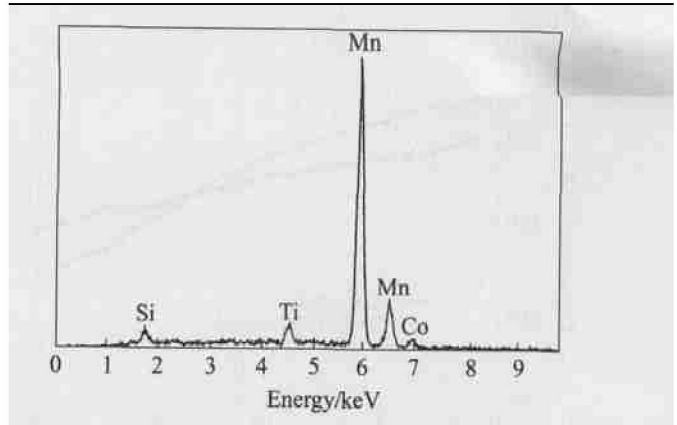


Fig. 3 EDS analysis of coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$

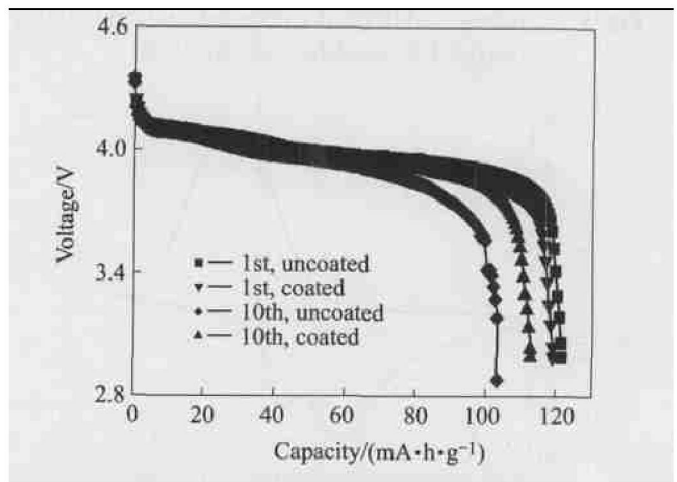


Fig. 4 Charge and discharge curves of uncoated and coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ powders at $25\text{ }^\circ\text{C}$ and at a current density of 0.1 mA/cm^2

relative to uncoated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$. But it can be found that the cycle performance of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ coated by $\text{SiO}_2\text{-TiO}_2$ has evidently been improved.

The electrochemical cycling behaviors of uncoated and $\text{SiO}_2\text{-TiO}_2$ coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ spinel at higher temperature of $55\text{ }^\circ\text{C}$ were examined, using a voltage range of $3.0\text{ - }4.35\text{ V}$ and a current density of 0.1 mA/cm^2 . The resulting data are plotted in Fig. 5. From the figure, it can be found that $\text{SiO}_2\text{-TiO}_2$ coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ has better cycling performance, though its initial specific capacity is slightly lower than that of uncoated one.

The uncoated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ loses about 16.22% of the initial discharge capacity ($123.38\text{ mA}\cdot\text{h/g}$) in 20 cycles. But the $\text{SiO}_2\text{-TiO}_2$ coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ exhibits much better behavior, it loses about 8.75% of its initial discharge capacity ($119.07\text{ mA}\cdot\text{h/g}$) during the same number of cycles. So, it is very safe to say that the $\text{SiO}_2\text{-TiO}_2$ surface treatment has improved the high temperature performance of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$.

In order to study the electrochemical performance of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ surface treated by $\text{SiO}_2\text{-TiO}_2$, another specific experiment was done. Fig. 6

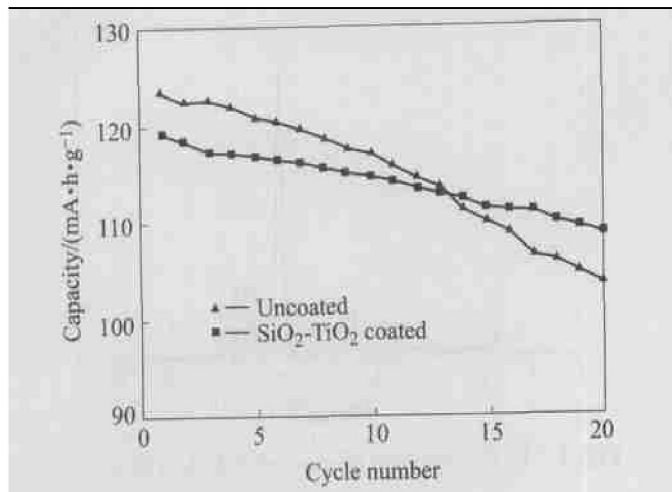


Fig. 5 Cycling stability of uncoated and $\text{SiO}_2\text{-TiO}_2$ coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ at $55\text{ }^\circ\text{C}$

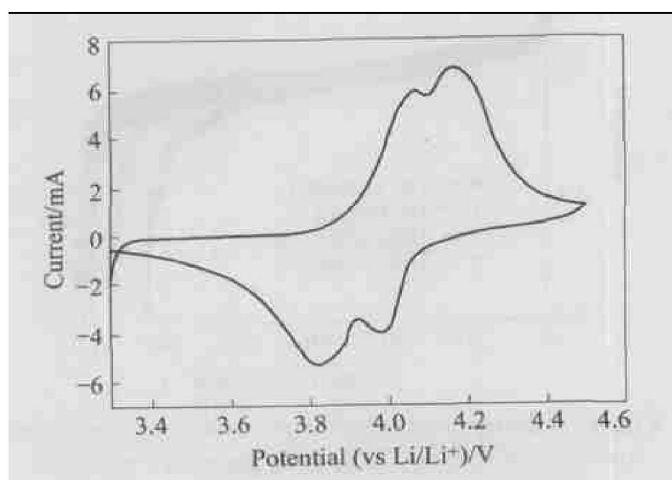


Fig. 6 First cyclic voltammetry curves of $\text{SiO}_2\text{-TiO}_2$ coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ at scan rate of 0.2 mV/s

shows the initial cyclic voltammetry curves of surface treated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ cycled between 3.3 V and 4.5 V at a scan rate of 0.2 mV/s . The cyclic voltammogram of surface treated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ sample presents two couples of peaks which represent two redox reactions for $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ ($4.08 - 4.01\text{ V}$, $4.16 - 3.84\text{ V}$). These two couples of peaks correspond to the typical two step reversible (de)intercalation process of lithium in surface treated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$.

It can be seen that the two couples of redox peaks change into one couple of peaks when the scan rate increases rapidly (Fig. 7). It is demonstrated that the reaction at $4.16 - 3.84\text{ V}$ is more stable than the others. This may influence the capacity when charge and discharge at an increased rate. Fig. 7 also indicates that the voltammogram plots of $\text{SiO}_2\text{-TiO}_2$ coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ in the first two cycles overlap each other completely. These demonstrate the improved structural stability of the material.

The $\text{SiO}_2\text{-TiO}_2$ coating prevents the direct

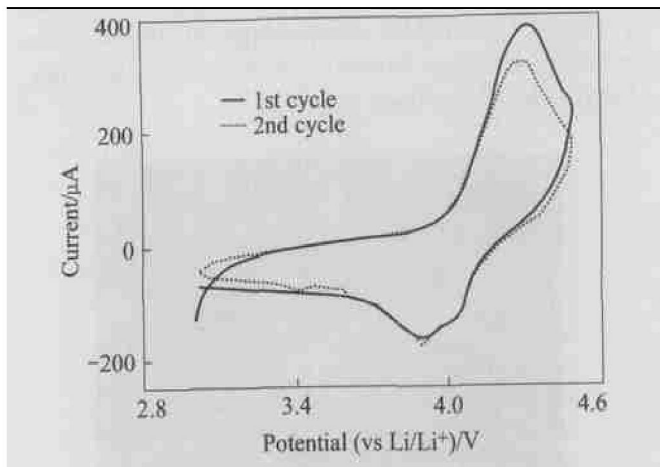


Fig. 7 1st and 2nd cyclic voltammetry curves of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ coated by $\text{SiO}_2\text{-TiO}_2$ at scan rate of 2 mV/s

contact of the spinel with the electrolyte, and suppresses Mn dissolution which is the principal cause of capacity loss. In this way, the $\text{SiO}_2\text{-TiO}_2$ layer functions primarily as a barrier coating.

4 CONCLUSIONS

The surface of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ was encapsulated with fine $\text{SiO}_2\text{-TiO}_2$ particles as a coating material for improving its cyclic properties at room temperature and elevated temperature. The initial specific capacity of coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ is slightly lower than that of uncoated one. The uncoated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ loses about 16.22% of the initial discharge capacity ($123.38\text{ mA}\cdot\text{h/g}$) in 20 cycles, while the $\text{SiO}_2\text{-TiO}_2$ coated $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ exhibits much better behavior, it loses about 8.75% of its initial discharge capacity ($119.07\text{ mA}\cdot\text{h/g}$) during the same number of cycles. The reason for the improved elevated temperature properties is that the surface coating reduces the dissolution of Mn, which results from the suppression of the electrolyte decomposition. The surface modification is an effective way to improve the electrochemical performance of $\text{LiCo}_{0.05}\text{Mn}_{1.95}\text{O}_4$ material for lithium ion batteries. The surface modification is successful in minimizing the harmful side reactions within the batteries by placing a protective barrier layer between cathode material and the liquid electrolyte.

REFERENCES

- [1] Ritchie A G. Recent developments and future prospects for lithium rechargeable batteries[J]. *J Power Sources*, 2001, 96: 1-4.
- [2] Scrosati B. Recent advances in lithium ion battery materials[J]. *Electrochimica Acta*, 2000, 45: 2461-2466.
- [3] Tarascon J M, Armand M. Issues and challenges facing rechargeable lithium batteries[J]. *Nature*, 2001, 414:

- 359 - 367.
- [4] Bauerlein P, Herr R, Kloss M, et al. Advanced lithium ion cells with lithium manganese spinel [J]. *J Power Sources*, 1999, 81 - 82: 585 - 588.
- [5] Iwata E, Takahashi K, Maeda K, et al. Capacity failure on cycling or storage of lithium ion batteries with LiMnO ternary phases having spinel framework structure and its possible solution [J]. *Journal of Power Sources*, 1999, 81 - 82: 430 - 433.
- [6] Jang D H, Oh S W. Electrolyte effects on spinel dissolution and cathodic capacity losses in 4V $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ rechargeable cells [J]. *J Electrochem Soc*, 1997, 144 (10): 3342 - 3348.
- [7] Aurbach D, Schechter A. Changes in the resistance of electrolyte solutions during contact with lithium electrodes at open circuit potential that reflect the Li surface chemistry [J]. *Electrochimica Acta*, 2001, 46(15): 2395 - 2400.
- [8] MacNeil D D, Dahn J R. The reaction of charged cathodes with nonaqueous solvents and electrolytes II. LiMn_2O_4 charged to 4.2V [J]. *J Electrochem Soc*, 2001, 148(11): A1211 - A1215.
- [9] Ostrovskii D, Ronci F, Scrosati B, et al. Reactivity of lithium battery electrode materials toward nonaqueous electrolytes: spontaneous reactions at the electrode-electrolyte interface investigated by FTIR [J]. *J Power Sources*, 2001, 103: 10 - 17.
- [10] Hsin L C, Cheng W H. Effects of cobalt-ion doping on the electrochemical properties of spinel lithium manganese oxide prepared via a reverse micelle route [J]. *Journal of the European Ceramic Society*, 2003, 23: 865 - 871.
- [11] Hwang B J, Santhanam R, Hu S G. Synthesis and characterization of multidoped lithium manganese oxide spinel, $\text{Li}_{1.02}\text{Co}_{0.1}\text{Ni}_{0.1}\text{Mn}_{1.8}\text{O}_4$, for rechargeable lithium batteries [J]. *J Power Sources*, 2002, 108: 250 - 255.
- [12] Yoshio M, Xia Y, Kumada N, et al. Storage and performance of Cr-modified spinel at elevated temperatures [J]. *J Power Sources*, 2004, 104: 79 - 85.
- [13] Amatucci G, Tarascon J M. Optimization of insertion compounds such as LiMnO_4 for Li ion batteries [J]. *J Electrochemical Soc*, 2002, 149(12): K31 - K46.
- [14] Amatucci G, Blyr A, Sigala C, et al. Surface treatments of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinels for improved elevated temperature performance [J]. *Solid State Ionics*, 1997, 104: 13 - 25.
- [15] LIU Zhao-lin, WANG Hong-bin, FANG Ling, et al. Improving the high-temperature performance of LiMn_2O_4 spinel by microemulsion coating of LiCoO_2 [J]. *J Power Sources*, 2002, 104: 101 - 107.
- [16] Sun Y K, Yoon C S, Oh I H. Surface structural change of ZnO-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel as 5V cathode materials at elevated temperatures [J]. *Electrochimica Acta*, 2003, 48: 503 - 506.

(Edited by YUAN Sai-qian)